

The As (Arsenic) System

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Equilibrium Diagram

The assessed As equilibrium diagram (Fig. 1) shows temperature-pressure phase relationships. The sublimation point is 614 °C (887 K) at 1.013 bar (1 atm) and the melting point is 817 °C (1090 K) at 36.3 ± 0.5 bar (35.8 ± 0.5 atm). The liquid-vapor and solid-vapor boundaries shown in the inset are based on the thermodynamic analysis discussed below (see "Thermodynamics" section). The only solid phase is α As, and the gas phase contains As_x ($x = 1, 2, 3, 4$), with $As_4(g)$ as the predominant species up to approximately 1127 °C (1400 K) (94% As_4 at 1127 °C).

Solid Phase

The crystal structure of As is rhombohedral, prototype α As; Pearson symbol $hR2$; space group $R\bar{3}m$; and Strukturbericht designation A7 [Pearson3]. Careful work of [65Tay] and [69Sch] yielded the crystallographic results in Table 1 for rhombohedral and equivalent hexagonal cells.

The hexagonal a parameter is independent of temperature, but the c parameter can be expressed as a function of temperature (t in °C) up to the melting point by:

$$c = 1.0534 (1 + 4.747 \times 10^{-5} t), \text{ nm} \quad (\text{Eq 1})$$

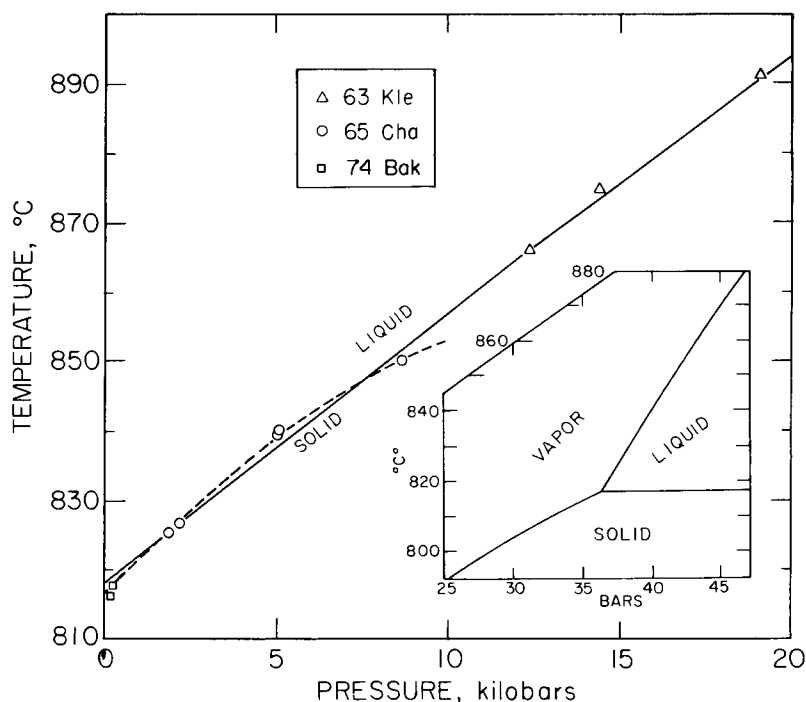
where the temperature coefficient is in excellent agreement with [60Kle]. The density is 5.73 g/cm^3 at 14 °C, according to [72Gra] and [84Wea]; hence, the gram atomic volume is $13.08 \text{ cm}^3/\text{g-atom}$. This volume (V in cm^3) as a function of temperature is expressed by using Eq 1:

$$V = 13.071 (1 + 4.747 \times 10^{-5} t) \text{ cm}^3/\text{g-atom} \quad (\text{Eq 2})$$

where t is in °C in the range up to the melting point.

α As is the only stable solid phase at pressures up to 70 kbar [63Kle] (probably somewhat higher) and up to its melting points. Well-annealed specimens do not show a first- or second-order transition, according to [65Tay]; a second-order phase transition observed by [60Kle] in the neighborhood of 227 °C (500 K) was probably due to improperly annealed specimens containing a non-equilibrium phase. Results of [65Tay] are in agreement with those of [22Las] up to 757 °C (1030 K). A phase transition reported by [22Las] at about 757 °C has not been observed by any other investigators [60Kle, 63Kle, 87Ode]. According to [72Dug], α As becomes tetragonal at 120 to 150 kbar and ambient temperatures, with $a = 0.8691$ and $c = 0.6363$ nm and

Fig. 1 Melting Temperature of α As vs Pressure



Inset shows P - T phase diagram for α As.

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As

Table 1 α As Lattice Parameter Data

Temperature, °C	Lattice parameters, nm			Angle α , degrees
	Equivalent hexagonal cell <i>a</i>	<i>c</i>	Rhombohedral cell <i>a</i>	
-268.8.....	0.37597	1.04412	0.41018	54.554
-195.....	0.37595	1.04573	0.41063	54.486
22.6.....	0.37598	1.0547	0.41318	54.133
26.....	0.37598	1.05475	0.41432	54.126
109.....	0.37599	1.0587	0.41432	53.967
209.....	0.37599	1.0635	0.41568	53.783
228.....	0.37601	1.0647	0.41603	53.733
250.....	0.37598	1.0658	0.41633	53.667
270.....	0.37599	1.0669	0.41665	53.633
297.....	0.37599	1.0682	0.41702	53.600
404.....	0.37595	1.0738	0.41860	53.367

$c/a = 0.732 \pm 0.001$. At 140 kbar, this phase becomes superconducting below 0.5 K [69Ber].

An orthorhombic form of As— ϵ As, isotypic with black phosphorus—obtained by distilling As-Hg and containing about 3 wt.% impurities, was characterized by [76Smi] as $a = 0.365$, $b = 0.447$, and $c = 0.11$ nm. It may be considered the parent form, from which an amorphous form is derived. A cubic form has also been reported [Pearson 1].

Solid-Gas Equilibria

The gas phase, in equilibrium with the solid phase, consists of As₄ (tetramer), with less than 0.19% by volume of As, As₂, and As₃, at 614°C (887 K) and less at lower temperatures. The sublimation temperature (at 1 atm) is 889 K from [09Jon], 889 K from [23Hor], 887 K from repeated determinations of [74Bak], 891 K from a representation of the data by [75Rau] as will be shown in the footnote to Table 5, 885 K from a compilation in [63Nes] (p 454), and 876 K in [Hultgren,E]. The selected value in this paper is $614 \pm 1^\circ\text{C}$ (887 ± 1 K), which will be further justified after an analysis of vapor pressure data. The solid-gas and the liquid-gas equilibria will be discussed in detail below (see "Thermodynamics" section).

Solid-Liquid Equilibria

The solid-liquid equilibria (melting points of α As) were determined carefully by [63Kle] up to 70 kbar by mechanical pressurization and thermal analysis. [65Cha] used argon as the pressure transmission medium, with greater accuracy at lower pressures. The data of [63Kle] and [65Cha] are plotted in Fig. 1, where the broken curve of [65Cha] up to 4 kbar is preferred in this assessment. Two points obtained by [74Bak] (816 °C at or below 101.3 bar of Ar and 818 °C at 202.6 bar of Ar) are also plotted in Fig. 1. Extrapolation of these data to 1.013 bar yields $817 \pm 1^\circ\text{C}$ (1090 K) as the melting point of the hypothetically existing

solid. Various other measurements are: 817 °C [14Gou], [23Hor], [75Rau], 818 °C [20Ras], 815 °C [21Hei], and 817 to 818 °C [82Rou]. This point is important in the determination of the triple point pressure, which is 36.3 bar (35.8 atm), as will be seen below.

The density of the liquid in g/cm³, measured by [63Mcg], is expressed by:

$$D = 5.80 - 0.000535 T \quad (\text{Eq 3})$$

where T is in K. The results of [60Kle] at 830 to 850 °C (1103 to 1123 K) are about 4% lower. The atomic volume of the liquid at 822 °C (1095 K) is 14.37 cm³/g-atom from Eq 3 under its own vapor pressure. The volume of solid from Eq 2 is 13.58 cm³/g-atom at the same temperature. Substitution of these values in the Clapeyron equation [75Gok] yields:

$$\begin{aligned} \Delta T/\Delta P &= (14.37 - 13.58)1095/23\,848 \times 9.999 \\ &= 0.0036 \text{ deg/bar} \end{aligned} \quad (\text{Eq 4})$$

where 23 848 is the enthalpy of fusion in J/g-atom and 9.999 cm³/J-g-atom is the conversion factor. The slope of the line in Fig. 1 at 822 °C (1095 K) is 0.002, and if instead, the atomic volume of liquid were taken to be 2.5% lower, then Eq 4 would also yield about 0.002. Greater accuracy from Eq 4 requires greater accuracy of atomic volumes. The decrease in the slope of the melting temperatures with increasing pressure shows that the volume difference between the liquid and the solid also decreases with increasing pressure.

Gas Phase

The density of gas was measured by [63Mcg] by vaporizing a known amount of As in a known volume of Vycor container, obtaining the following equation for the density (D) in g/cm³ at the point where the condensed phase disappeared:

$$\begin{aligned} D &= 0.2072 - 6.182 \times 10^{-4} T + 5.043 \times 10^{-7} T^2 \\ &\pm 0.0007 \end{aligned} \quad (\text{Eq 5})$$

where T is the temperature in K.

The values of pressure were computed from [23Hor] by [63Mcg]. The compressibility factors ($Z = PV/RT$) computed from his values are listed in the third column of Table 2.

The compressibility factors, calculated from the equations of state obtained by [75Rau], are in the last column of Table 2. It is clear that the sets of results from [63Mcg] and [75Rau] are discordant. (Less precise values of [82Rou] indicated $Z = 0.88$ to 1.02 at 817 °C.) The present author, based on his experience, believes that the dimensional stability of silica and Vycor above 827 °C decreases with increasing pressure difference, so that the volume of the containers used in nearly all the experiments were subject to change. Further, silica begins to devitrify above 1027 °C, and on cooling, it has a tendency to crumble; consequently, the volume of the silica container cannot be rechecked after devitrification. Therefore, the values of Z in

Table 2 Compressibility Factor (Z) for As₄(g)

Temperature, °C	Pressure, bar	Compressibility factor, Z	
		[63Mcg]	[75Rau]
727.....	8.2	...	0.949
817.....	36.3	0.905	0.821
877.....	47.4	0.911	0.799
927.....	58.4	0.915	0.781
1027.....	84.3(a)	0.914	0.752

Note: $Z = PV/RT$.
(a) Gas phase contains about 97% As₄ by volume at 1027 °C.

Table 2 are questionable, and $Z = 1$ is adopted in this assessment.

Metastable Phases

Three amorphous forms (β , γ , and δ) are differentiated by X-ray diffraction pattern [Pearson1, Pearson2]. Above 287 °C (560 K), these forms transform into α As. Differential thermal analysis of γ As was carried out by [66Ben] to show that its transformation to α As is sharp and irreversible, with 7820 J/g-atom at 288 ± 3 °C (561 ± 3 K) as the irreversible enthalpy of transition.

Thermodynamics

Heat Capacity of Solid and Related Properties

The heat capacity of solid, $C_p^0(c,\alpha)$, in the range of 0.7 to 4 K was measured by [67Cul] and expressed as:

$$10^5 C_p^0 = 19.41 T + 8.79 T^3 + 0.0552 T^5 \text{ (J/g-atom}\cdot\text{K)} \quad (\text{Eq 6})$$

where T is in K. The first term on the right ($19.41 T$) is the electronic contribution to C_p^0 .

The heat capacity from 13.9 to 289.12 K was measured by [69Pau], whose results also contained those of [66Nog]. The earlier results of [30And] covered a narrower range—57 to 291 K. All sets of data scatter much more than those obtained by the usual accuracy of calorimeters in the range 260 to 290 K, indicating either a possible incomplete phase transition or the presence of a nonequilibrium phase.

The presence of about 10% or less of a nonequilibrium phase is difficult to detect by X-ray, and the transition of this amount might possibly account for the scatter. The heat capacity results of [69Pau] were corrected slightly for the atomic weight of As and plotted with those of [66Nog] and [30And]; the data were read from a large-scale smooth curve at convenient intervals and listed in Table 3, along with selected results of [67Cul]. Most of the data above 13 K are those of [69Pau], who achieved a greater degree of accuracy.

The resulting value of $S^0(298) = 35.564$ J/g-atom·K is within the 35.631 ± 0.063 J/g-atom·K reported by

Table 3 Assessed Values of Standard Heat Capacity C_p^0 at Low Temperatures for α As

Temperature, K	Heat capacity, J/g-atom·K	Temperature, K	Heat capacity, J/g-atom·K
1.....	0.000285	90.....	15.330
5.....	0.01368	100.....	16.598
10.....	0.1121	120.....	18.552
15.....	0.477	140.....	20.041
20.....	1.155	160.....	21.125
25.....	2.109	180.....	21.836
30.....	3.201	200.....	22.422
35.....	4.431	220.....	22.891
40.....	5.590	240.....	23.313
50.....	7.933	260.....	23.707
60.....	10.188	280.....	24.066
70.....	12.242	298.15.....	24.393
80.....	13.853		

Note: $S^0(298) = 35.564 \pm 0.29$ J/g-atom·K; $H^0(298) - H^0(0) = 5104 \pm 20$ J/g-atom.

[69Pau], the 35.02 ± 0.04 J/g-atom·K by [66Nog], and the 35.1 ± 0.8 J/g-atom·K by [30And]. A reinvestigation using well-characterized and annealed specimens is necessary to achieve a better accuracy in C_p^0 and S^0 .

The heat capacity at high temperatures has not been investigated with a satisfactory degree of precision. The earliest values by [22Las] are much too low at low temperatures and much too high at high temperatures—2.18 J/g-atom·K at 298.15 K and 37.61 J/g-atom·K at 1000 K. Results prior to 1960 were summarized as $C_p^0 = 21.88 + 0.00929 T$ by [60Kel], yielding 24.64 J/g-atom·K at 298.15 K, in fair agreement with the value in Table 3. The more recent values were reported by [60Kle]. The value at about 620 K from the enthalpy curve of [60Kle] is $C_p^0 = 25.5$ J/g-atom·K. The mean heat capacity values listed in their table were plotted as $C_p^0 \Delta T$ vs T by this author and fitted in a cubic equation, with the requirement that $C_p^0(298) = 24.393$ J/g-atom·K from Table 3 be satisfied; the derived result for C_p^0 is:

$$C_p^0(\alpha\text{As}) = 23.221 + 0.003933 T, \text{ J/g-atom}\cdot\text{K} \quad (\text{Eq 7})$$

where T is in K.

Thermodynamic data obtained with this equation and the data in Table 3 are listed in Table 4.

Heat Capacity of Liquid

The heat capacity of liquid As, reported by [60Kle] in a plot, follows an unusual path, decreasing by a factor of approximately three from the melting point to 1150 K. It is not clear whether the presence of considerable amounts of vapor phase had any effect on these results. A careful analysis of data for other elements by [78Ita] suggested that $C_p^0(L) - C_p^0(c,\alpha) = 1.30$ J/g-

As

Table 4 Thermodynamic Properties of Solid α As and Liquid As at High Temperatures Under Equilibrium Pressure

Temperature, K	Heat capacity, J/g-atom·K	Entropy, J/g-atom·K	Gibbs energy function(a), J/g-atom·K	Relative enthalpy(b), J/g-atom
Solid αAs				
298.15	24.393	35.564	35.564	0
300	24.401	35.715	35.564	46
400	24.794	42.790	36.526	2 506
500	25.188	48.363	38.355	5 004
600	25.581	52.990	40.417	7 544
700	25.974	56.965	42.505	10 121
800	26.368	60.459	44.539	12 736
887	26.711	63.195	46.233	15 046
900	27.761	63.584	46.480	15 393
1000.....	27.154	66.425	48.334	18 092
1090.....	27.510	68.781	49.928	20 548
Liquid As				
1090.....	28.83	90.659	49.928	44 396
1100.....	28.83	90.923	50.300	44 685
1200.....	28.83	93.433	53.794	47 568
1300.....	28.83	95.738	56.932	50 451
1400.....	28.83	97.876	59.781	53 333
1500.....	28.83	99.864	62.388	56 216

Note: Values for the liquid are estimates. (a) $(G^0 - H^0(298))/T \equiv G^0_f$. (b) $H^0 - H^0(298)$ where $H^0(298)$ refers to α As; $H^0(298) - H^0(0) = 5104$ J/g-atom.

Table 5 Enthalpy of Fusion of α As at 1090 K

Reference	Method	Enthalpy of fusion, J/g-atom
[60Kle]	Calorimetry	21 760
[74Bak]	Differential thermal analysis	25 100
[82Rou]	Differential thermal analysis	24 200
[23Hor]	Difference in slopes of $\ln P$ vs $1/T$	23 900(a)
[74Bak]	Difference in slopes of $\ln P$ vs $1/T$	23 920(b)
[75Rau]	Difference in slopes of $\ln P$ vs $1/T$	25 170(c)
Average	24 000
Assessed	23 848 \pm 1600

(a) From $\ln P$ (atm, sub) = 19.065 - 16 940/ T and $\ln P$ (atm, vapn) = 15.384 - 5641/ T . (b) From $\ln P$ (atm, sub) = 19.217 - 17 046/ T and $\ln P$ (atm, vapn) = 8.655 - 5538/ T . (c) From $\ln P$ (atm, sub) = 19.621 - 17 480/ T and $\ln P$ (atm, vapn) = 8.510 - 5370/ T .

atom·K at the melting point, from which $C_p^0(L) = 28.83$ J/g-atom·K is obtained, as listed in Table 4.

Direct experimental results of higher precision are necessary to obtain reliable thermodynamic data for liquid As.

Enthalpy and Entropy of Fusion

The enthalpy of fusion data obtained by various investigators are shown in Table 5. The value accepted here is $\Delta_{fus}H = 23\,848 \pm 1600$ J/g-atom at 1090 K. The entropy of fusion is $\Delta_{fus}S = 21.878 \pm 1.55$ J/g-atom·K at 1090 K.

Calculations of condensed multicomponent phase diagrams require the standard Gibbs energy of fusion as a function of temperature. The foregoing data for the heat capacity change for fusion, $C_p^0(L) - C_p^0(c,\alpha) = 1.30$ J/g-atom·K and $H^0(L, 1090) - H^0(c,\alpha, 1090) = 23\,848$ J/g-atom·K, yield:

$$\Delta_{fus}G^0/RT = \ln a_{c,\alpha}/a_L = 2698.3/T - 0.156 \ln T - 1.3844 \quad (\text{Eq 8})$$

where T is in K, and $a_{c,\alpha}$ and a_L are the activities of As in the coexisting solid and liquid phases, respectively. For the As-rich corner of a phase diagram, $a_{c,\alpha}/a_L$ is closely approximated by the corresponding ratio of atomic fractions $x_{c,\alpha}/x_L$.

Sublimation and Vaporization

The standard enthalpies of sublimation ($\Delta_{sub}H^0$), based on vapor pressure measurements by various methods, are summarized in Table 6. The pressure data in atm (1 atm = 1.01325 bar) in the range of 715 to 1396 K are plotted in Fig. 2. The sublimation pressures at temperatures below 700 K determined by the effusion techniques scatter to a considerable degree. A plot of such data prior to 1963 was given by [63Nes] and need not be presented here with the more recent data, because it is generally agreed that the effusion techniques yield less reliable data than the direct measurements [55Bre, 63Nes, Hultgren,E]. (The rates of sublimation have been investigated by [68Ros], [70Ros], [76Ros], and [77Kle].) The vaporization coefficient of $As_4(g)$ is very low— 5×10^{-4} by [55Bre] and about $(\exp - 5500/T)$ by [68Ros]; therefore, the effusion investigations were considered to be less reliable by [55Bre], [63Nes], and [Hultgren,E] than direct manometric investigations, despite careful work of [63Nes], [68Ros], [68Her], and [71Mal], among others.

The first set of highly reliable data by direct observation of pressure was obtained by [23Hor]. Later, [74Bak], [75Rau], and [82Rus] refined and extended the results of [23Hor]. Earlier data by [19Ruf] are in disagreement with [21Ruf] from the same laboratory, and it is assumed here that [21Ruf] supersedes [19Ruf]. The data prior to 1921 are arbitrarily excluded in the averaging process, because they are considered to be less reliable. The selected value of $39\,137 \pm 200$ J/g-atom is the best fitting $\Delta_{sub}H^0(298)$ value satisfying the results of investigations plotted in Fig. 2.

Inclusion of all the data in the averaging process would change this value slightly. However, even a change of ± 85 J in 39 137 would have a significant effect on the atmospheric sublimation temperature and the triple point pressure of As. Further, the errors in C_p^0 for α As also would have a significant impact on $\Delta_{\text{sub}}H^0(298)$.

The optimum equation for $C_p^0(c,\alpha)$ was obtained by iteration on a computer so that: (1) $C_p^0 = 24.393$ J/g-atom·K for α As at 298.15 K was satisfied; (2) the mean heat capacities reported by [60Kle] were used as a strong guideline; and (3) the concordant vapor pressures in Fig. 2 were well represented by the resulting Gibbs energy functions $(G^0 - H^0(298))/T$. It is believed that $C_p^0(c,\alpha)$ is the least accurately determined property, and its adjustment is the logical procedure for the representation of overall data. An alternative method is to make adjustments in the thermodynamic properties of gaseous As₄, a procedure presented by

[82Rus], which yields $\Delta_{\text{sub}}H^0(298) = 39\,170$ J/g-atom in very close agreement with our value of 39 137 J/g-atom. It is certain that new measurements of $C_p^0(c,\alpha)$ are essential for deciding where the necessary adjustments should be made.

Dissociation of As₄(g) into As₂(g)

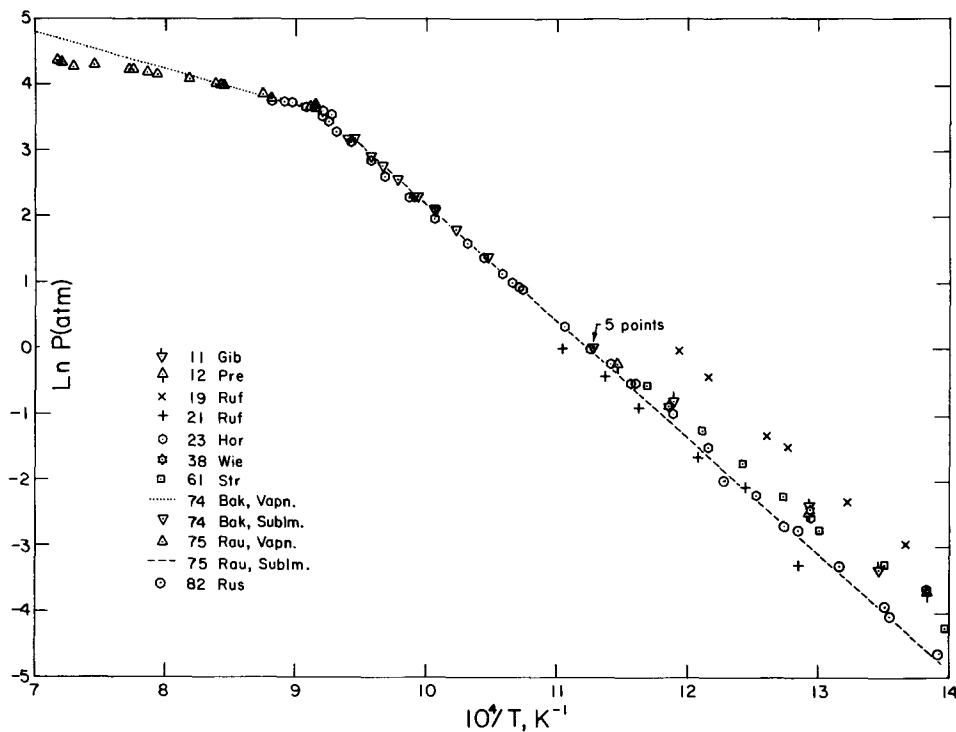
[67Art] showed that spurious As₄(g) caused inaccuracy in the data for the dissociation of As₄(g)—As₄(g) → 2As₂(g)—determined by mass spectroscopy, but his results were somewhat high. [73Mur] showed conclusively that earlier results by effusion-mass spectrometry [58Dro, 59Gol, 59Gut, 61Gut, 67Art, 69Hud, 70Dem], summarized as $\Delta_r H(298) = 288\,700$ J/reaction in [Hultgren,E] are in error. A “see-through” ion source and a liquid nitrogen-cooled condensation plate eliminated the spurious As₄(g), and thus [73Mur] obtained 227 020 J/reaction listed in

Table 6 Standard Enthalpy of α As Sublimation at 298.15 K, As(c, α) = 0.25 As₄(g)

Reference	Temperature, K	Method	Enthalpy of sublimation, J/g-atom
[11Gib, 23LBT]	743 to 842	Quartz spiral gauge	38 500
[12Pre]	673 to 873	Quartz spiral gauge	38 250
[19Ruf]	732 to 838	Boiling point observation	37 300
[21Ruf]	778 to 906	Boiling point observation	39 760
[23Hor]	723 to 1126	Quartz spiral gauge	39 160
[38Wie]	773 to 863	Quartz spoon gauge	38 850
[55Bre]	575	Knudsen effusion	38 440(a)
[61Str]	715 to 856	Quartz spoon gauge	38 690
[63Nes]	390 to 573	Knudsen effusion	39 540
[68Ros]	494 to 575	Knudsen effusion	38 410
[68Her]	522 to 714	Torsion effusion	39 820
[71Mal]	563 to 630	Knudsen effusion	39 880
[74Bak]	1090 to 1370	Argon as pressure transmitter	39 020(b)
	886 to 1064	Argon as pressure transmitter	39 170
[75Rau]	1058 to 1223	Quartz spiral gauge	39 090(c)
	816 to 1090	Quartz spiral gauge	39 270(d)
[77Mal]	790 to 857	Complete sublimation(e)	39 090
[82Rus]	679 to 814	Quartz Bourdon gauge	39 240(f)
Assessed	(g)		39 137 \pm 200

(a) Results for the average of two highest pressures, 3.3×10^{-5} bar, with the smallest orifices, at 575 K. (b) Calculated from his equation for vaporization at average $T = 1230$ K, $P = 64.48$ bar, and $(G^0 - H^0(298))/T$ of this paper. (c) Result from six points for vaporization up to 1223 K; the results from 1260 to 1396 K deviate systematically from linearity in $\ln P$ vs $1/T$, and As₄ begins to dissociate into other species; further, according to [75Rau], deviations from ideal gas behavior exist. (d) From $\ln P = 19.621 - 17\,480/T$ representing his linear plot for the untabulated data and using $\ln P$ at the average $T = 953$ K with this author's ΔG_{f} . (e) Observation of complete sublimation of known masses of As into a known volume at a known temperature and use of $PV = RT$. (f) Value calculated without using two very low pressures below 1 torr (0.0014 bar) where the accuracy is low. (g) Data by [71Mam], obtained by using a quartz membrane null manometer at 630 to 1270 K, presumably yielding 31 485 J/g-atom, could not be checked by this author because their data columns are jumbled. Likewise, $\Delta H^0(298)$ for As₄(g) → 2As₂(g) as 221 752 J, though in reasonable agreement with the existing data, could not be verified. Further, $\Delta_{\text{sub}}H(298)$ of 44 978 J/g-atom by mass spectrometry of [64Wes] and 33 472 J/g-atom by effusion technique of [72Kaz] are not included in this table, because they lie outside the range of tabulated data. Assessed value is also average of all ten direct values since 1920.

Fig. 2 Sublimation and Vaporization Pressures of As vs Temperature



A datum point of [23Hor] and one of [75Rau] for supercooled liquid are not shown.

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Table 7 Enthalpy of Dissociation for $\text{As}_4(\text{g}) \rightarrow 2\text{As}_2(\text{g})$

Reference	Temperature, K	Method	Enthalpy of dissociation, J/reaction at 25 °C
[71Mam](a)	630 to 1270	Quartz membrane null manometer	225 520 ± ?
[73Mur]	807 to 1050	Mass spectrometry	227 020 ± 2900
[74Pup]	918.5 to 1084	Mass spectrometry	227 610 ± 6300
[75Rau]	...	Vapor density measurements	224 850 ± 4200
[77Mal]	1006 to 1217	UV spectra	230 290 ± 7100
[78Dro]	689 to 1008	Mass spectrometry	226 770 ± 5800
Assessed	227 042 ± 3300(b)

Note: $\Delta_f H^0(298)$ for $2\text{As}(\text{c}, \alpha) \rightarrow \text{As}_2(\text{g}) = 191\,795 \pm 2100$ J/mol.

(a) Result cannot be verified; see footnote (g) to Table 6. However, this value is consistent with their $\log [P^2(\text{As}_2)/P(\text{As}_4)] = 8.919 - 11\,800/T$, where P is in atm. (b) A value of 191 630 J/reaction by [74Fox] is too low and not included in this table. An indirectly computed value from total pressure and gas density over GaAs by [73Vig] is 7280 J/reaction lower than 227 042 J/reaction and outside the values listed in this table.

Table 7. This result was obtained from $\text{As}_4(\text{g})$ emanating from MoAs_2 and Mo_2As_3 .

Using the same method with InAs, [74Pup] confirmed very closely the previous value of [73Mur]. [75Rau] determined equilibrium concentrations of As_2 and As_4

from vapor density measurements and obtained $\Delta_r H^0(298) = 224\,850 \pm 4200$ J/reaction after making corrections for deviations from ideal gas behavior. [78Dro] determined the equilibria in $\text{As}_4 \rightarrow 2\text{As}_2$ by mass spectrometry and obtained $\Delta_r H^0(298) = 226\,770 \pm 5800$ J/reaction. The procedure in the experiments

Table 8 Thermodynamic Properties of As in Its Usual Standard States of Pure α As up to 887 K and 1/4 As₄(g) above 887 K at 1.013 bar

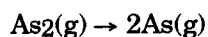
Temperature, K	Heat capacity, J/g-atom·K	Entropy, J/g-atom·K	Gibbs energy function (a), J/g-atom·K	Enthalpy, J/g-atom
Pure αAs				
298.15.....	24.393	35.564	35.564	0
300.....	24.401	35.715	35.564	46
400.....	24.794	42.790	35.526	2 506
500.....	25.188	48.363	38.355	5 004
600.....	25.581	52.990	40.417	7 544
700.....	25.974	56.965	42.505	10 121
800.....	26.368	60.459	44.539	12 736
887.....	26.711	63.195	46.233	15 046
1/4 As₄(g)				
887.....	20.606	103.809	46.233	51 070
900.....	20.610	104.110	47.070	51 338
1000.....	20.644	106.282	52.882	53 400
1090.....	20.669	108.064	57.367	55 262
1100.....	20.669	108.253	57.827	55 467
1200.....	20.686	110.052	62.107	57 534
1300.....	20.698	111.709	65.860	59 605
1400.....	20.711	113.244	69.191	61 676
1500.....	20.719	114.671	72.174	63 747

(a) $[G^0 - H^0(298)]/T \equiv G_{ef}$. (b) Values for $H^0 - H^0(298)$; $H^0(298) - H^0(0) = 5104$ J/g-atom.

of [78Dro] also eliminated spurious As₄(g), because the experimental *interception* of the molecular beam from the Knudsen cell completely suppressed the signal for the effusing species. The assessed value of $227\,042 \pm 3300$ J/mol of As₄ is the average value, which combined with $\Delta_f H^0(\text{As}_4, 298) = 156\,548$ J/mol As₄ yields $\Delta_f H^0(\text{As}_2, 298) = 191\,795 \pm 2100$ J/mol of As₂.

Dissociation of As₂(g) into As(g)

The following dissociation reaction and its $\Delta_r H(298)$ were investigated by optical spectroscopy by [37Kin]:



$$\Delta_r H(298) = 382\,500 \pm 2260 \text{ J/reaction}$$

as calculated by Rosenblatt in [Hultgren,E]. Mass spectrometric investigations of [73Kor] with gadolinium arsenide at 1323 to 1901 K yielded $\Delta_r H(298) = 382\,000 \pm 10\,500$ J/reaction, in close agreement with [37Kin]. A value computed from total pressure and gas-density over GaAs by [73Vig] is 12 720 J higher than 382 400 J and not considered in selecting an acceptable value in this assessment. The adopted value is $\Delta_r H(298) = 382\,418 \pm 2500$ J/reaction, and this value, combined with $\Delta_f H^0(\text{As}_2, \text{g}, 298) = 191\,795$ J/mol, yields $\Delta_f H^0(\text{As}, \text{g}) = 287\,100 \pm 2500$ J/mol for As(c, α) \rightarrow As(g). Atomic absorption spectrometry of As(g) in equilibrium with the solid at 633 to 693 K by [78Mur] would lead to a very low value of about 181 170 J/mol, which is not considered in the present evaluation. The value compiled by [Hultgren,E] is $301\,750 \pm 2300$

Table 9 Thermodynamic Properties of Ideal Monatomic Gas As(g) in its Standard State

Temperature, K	Heat capacity, J/mol·K	Entropy, J/mol·K	Gibbs energy function, J/mol·K	Enthalpy(a), J/mol	Enthalpy of formation, J/mol	Gibbs energy of formation, J/mol	Equilibrium constant, log K _p
For As(c, α) \rightarrow As(g)							
298.15.....	20.786	174.100	174.10	0	287 100	245 796	-43.062
300.....	20.786	174.230	174.105	38	287 092	245 537	-42.751
400.....	20.786	180.209	174.916	2 117	286 711	231 743	-30.262
500.....	20.786	184.845	176.452	4 197	286 293	218 052	-22.779
600.....	20.786	188.636	178.176	6 276	285 832	204 445	-17.798
700.....	20.786	191.841	179.912	8 351	285 330	190 917	-14.246
800.....	20.786	194.615	181.577	10 431	284 795	177 471	-11.588
887.....	20.786	196.761	182.962	12 238	284 293	165 820	-9.765
For 1/4 As₄(g) \rightarrow As(g)							
887.....	20.786	196.761	182.962	12 238	248 269	165 820	-9.765
900.....	20.786	197.066	183.167	12 510	248 273	164 613	-9.554
1000.....	20.786	199.255	184.665	14 590	248 290	155 317	-8.113
1090.....	20.790	201.050	185.954	16 456	248 294	146 939	-7.041
1100.....	20.790	201.238	186.088	16 665	248 298	146 015	-6.934
1200.....	20.744	203.045	187.426	18 744	248 311	136 719	-5.951
1300.....	20.803	204.711	188.694	20 824	248 319	127 416	-5.120
1400.....	20.820	206.254	189.891	22 907	248 331	118 117	-4.407
1500.....	20.845	207.690	191.033	24 987	248 340	108 812	-3.789

(a) Values for $H^0 - H^0(298)$; $H^0(298) - H^0(0) = 6197$ J/mol.

As

Table 10 Thermodynamic Properties of Ideal Diatomic Gas As₂(g) in its Standard State

Temperature, K	Heat capacity, J/mol·K	Entropy, J/mol·K	Gibbs energy function, J/mol·K	Enthalpy(a), J/mol	Enthalpy of formation, J/mol	Gibbs energy of formation, J/mol	Equilibrium constant, log K _p
For 2As(c,α) → As₂(g)							
298.15.....	35.003	240.772	240.772	0	191 795	141 214	-24.740
300.....	35.012	240.990	240.772	67	191 769	140 900	-24.532
400.....	35.957	251.207	242.149	3 623	190 405	124 156	-16.213
500.....	36.443	259.291	244.785	7 247	189 030	107 755	-11.257
600.....	36.727	265.960	247.789	10 904	187 611	91 621	-7.976
700.....	36.903	271.634	250.797	14 585	186 138	75 747	-5.652
800.....	37.020	276.571	253.714	18 284	184 606	60 082	-3.923
887.....	37.091	280.395	256.144	21 510	183 213	46 614	-2.745
For 1/2 As₄(g) → As₂(g)							
887.....	37.091	280.395	256.144	21 510	111 165	46 614	-2.745
900.....	37.104	280.939	256.504	21 991	111 110	45 664	-2.650
1000.....	37.162	284.847	259.149	25 698	110 692	38 409	-2.006
1090.....	37.200	288.039	261.387	29 050	110 324	31 941	-1.531
1100.....	37.204	288.395	261.646	29 422	110 282	31 204	-1.482
1200.....	37.238	291.633	264.019	33 137	109 863	24 029	-1.046
1300.....	37.263	294.616	266.261	36 861	109 445	16 887	-0.679
1400.....	37.284	297.378	268.387	40 589	109 031	9 786	-0.365
1500.....	37.300	299.955	270.412	44 317	108 617	2 699	-0.094

(a) Values for $H^0(g) - H^0(298)$; $H^0(298) - H^0(0) = 9422$ J/mol.

Table 11 Thermodynamic Properties of Ideal Triatomic Gas As₃(g) in its Standard State

Temperature, K	Heat capacity, J/mol·K	Entropy, J/mol·K	Gibbs energy function, J/mol·K	Enthalpy(a), J/mol	Enthalpy of formation, J/mol	Gibbs energy of formation, J/mol	Equilibrium constant, log K _p
For 3As(c,α) → As₃(g)							
298.15.....	59.045	310.122	310.122	0	243 509	182 858	-32.035
300.....	59.070	310.486	310.122	109	243 480	182 477	-31.771
400.....	60.413	327.695	312.478	6 088	242 078	162 348	-21.200
500.....	61.091	341.251	316.900	12 175	240 672	142 591	-14.896
600.....	61.467	352.423	321.921	18 301	239 178	123 106	-10.717
700.....	61.693	361.924	326.975	24 464	237 609	103 889	-7.752
800.....	61.844	370.171	331.871	30 639	235 940	84 906	-5.544
887.....	61.944	376.560	335.946	36 024	234 396	68 551	-4.037
For 3/4 As₄(g) → As₃(g)							
887.....	61.944	376.560	335.946	36 024	126 323	68 551	-4.037
900.....	61.957	377.464	336.544	36 828	126 323	67 705	-3.929
1000.....	62.032	383.991	340.963	43 028	126 336	61 191	-3.196
1090.....	62.078	389.334	344.736	48 610	126 336	55 333	-2.652
1100.....	62.082	389.903	345.151	49 229	126 336	54 677	-2.596
1200.....	62.132	395.313	349.113	55 442	126 348	48 158	-2.096
1300.....	62.170	400.287	352.862	61 655	126 348	41 639	-1.673
1400.....	62.199	404.894	356.414	67 873	126 353	35 125	-1.310
1500.....	62.224	409.187	359.791	74 094	126 361	28 606	-0.996

Note: Heat capacity and related properties are estimates. (a) Values for $H^0 - H^0(298)$; $H^0(298) - H^0(0) = 14 799$ J/mol.

J/mol, and that of [87Bre] is 285 190 J/mol; the latter is reasonably close to the adopted value.

Gaseous Triarsenic, As₃(g)

[69Hüd] investigated $As_3(g) \rightarrow As_2(g) + As(g)$ by electron impact and obtained $\Delta_r H(298) = 261 330 \pm 29 000$ J/reaction (see also [Hultgren,E]).

Combination of this value with $\Delta_f H^0(298)$ for As₂(g) and for As(g) from the preceding sections yields $\Delta_f H^0(As_3,g, 298) = 217 600 \pm 33 500$ J/mol. The value summarized in [Hultgren,E] is 261 420 ± 37 700 J/mol, and that of [87Bre] is 216 170 J/mol. Electron impact of As₄(g) by [73Ben] in the range of 653 to 693 K yielded $\Delta_f H^0(298) = 243 500 \pm 21 000$ J/mol of As₃.

Table 12 Thermodynamic Properties of Ideal Tetratomic Gas As₄(g) in its Standard State

Temperature, K	Heat capacity, J/mol·K	Entropy, J/mol·K	Gibbs energy function, J/mol·K	Enthalpy(a), J/mol	Enthalpy of formation, J/mol	Gibbs energy of formation, J/mol	Equilibrium constant, log K _p
For 4As(c,α) → As ₄ (g)							
298.15	77.220	327.323	327.323	0	156 549	101 370	-17.759
300	77.237	327.808	327.335	142	156 507	101 018	-17.589
400	79.730	350.418	330.377	8 017	154 540	82 835	-10.817
500	80.919	368.343	336.243	16 050	152 582	65 137	-6.805
600	81.588	383.171	342.866	24 184	150 557	47 831	-4.164
700	81.990	395.773	349.556	32 351	148 415	30 878	-2.304
800	82.257	406.735	356.025	40 568	146 172	14 251	-0.931
887	82.416	415.237	361.426	47 731	144 097	0	0
For As ₄ (g) as the standard state							
887	82.416	415.237	361.426	47 731
900	82.442	416.442	362.217	48 802
1000	82.575	425.128	368.075	57 053
1090	82.667	432.257	373.087	64 492
1100	82.676	433.011	373.627	65 321
1200	82.743	440.207	378.882	73 588
1300	82.793	446.834	383.857	81 873
1400	82.843	452.977	388.581	90 157
1500	82.877	458.688	393.062	98 441

(a) Values for $H^0 - H^0(298)$; $H^0(298) - H^0(0) = 17 539$ J/mol.

Table 13 Standard Thermodynamic Properties of As₄(g) in Equilibrium with Solid and Liquid As

Temperature, K	Heat capacity, J/mol·K	Entropy, J/mol·K	Gibbs energy function, J/mol·K	Enthalpy(a), J/mol	Enthalpy of formation, J/mol	Gibbs energy of formation, J/mol	Equilibrium constant, log K _p
For 4As(c,α) → As ₄ (g)							
298.15	77.220	327.323	327.323	0	156 548	101 370	-17.759
300	77.237	327.808	327.335	142	156 507	101 018	-17.589
400	79.730	350.418	330.377	8 017	154 540	82 835	-10.817
500	80.919	368.343	336.243	16 050	152 582	65 137	-6.805
600	81.588	383.171	342.866	24 184	150 557	47 831	-4.164
700	81.990	395.773	349.556	32 351	148 415	30 878	-2.304
800	82.257	406.735	356.025	40 568	146 172	14 251	-0.931
887	82.416	415.237	361.426	47 731	144 097	0	0
900	82.442	416.442	362.217	48 802	143 779	-2 117	0.123
1000	82.575	425.128	368.075	57 053	141 235	-18 192	0.950
1090	82.667	432.257	373.087	64 492	138 850	-32 426	1.554
For 4As(L) → As ₄ (g)							
1090	82.667	432.257	373.087	64 492	43 455	-32 426	1.554
1100	82.676	433.011	373.627	65 321	43 129	-33 121	1.573
1200	82.743	440.207	378.882	73 588	39 865	-39 907	1.737
1300	82.793	446.834	383.857	81 873	36 618	-46 426	1.865
1400	82.843	452.977	388.581	90 157	33 372	-52 689	1.966
1500	82.877	458.688	393.062	98 441	30 125	-58 722	2.045

(a) $H^0(298) - H^0(0) = 17 539$ J/mol. Standard state for liquid in this table is assumed to be the pure liquid under its equilibrium pressure As₄(g) at 1090 to 1500 K.

(The original value, 241 000 J/mol, has been corrected slightly in this paper for the enthalpy of sublimation of As(c,α).) The author in consultation with [87Hud] and [87Mar] selected $\Delta_f H^0(298) = 243 509 \pm 21 000$ J/mol (58 200 cal/mol) for the formation of triarsenic gas, because the result of [73Ben] is considered to be more reliable than that of [69Hud] as stated by [87Hud].

Heat Capacities and Related Properties of Gaseous Species

Thermal properties of monatomic As(g) are from [64Hil]. The values for diatomic As₂(g) are from the vibrational frequency of [37Kin] by emission spectroscopy and rotational constant of [68Per] by

As

spectroscopy as calculated and listed by Rosenblatt in [Hultgren,E]. (See also [69Per], [70Per], and [80Per].) All the gas properties of triatomic $\text{As}_3(\text{g})$ are estimates by [69Hud] and are also listed in [Hultgren,E]. The results for As, As_2 , and As_3 are listed in Tables 9, 10, and 11.

The properties of the tetramer $\text{As}_4(\text{g})$ calculated by [68Her] were revised by [70Cap] and [72Bru], based on their infrared and Raman spectroscopy. The resulting values of $S^0(298)$ are 329.841 [68Her], 327.31 [70Cap], and 327.15 J/mol·K [72Bru]. A previous value of [69Ozi], derived from his spectroscopic data is 328.40 J/mol·K. Based on these investigations, $S^0(298) = 327.323 \pm 1.3$ J/mol·K in [Hultgren,E] is adopted, as suggested by [87Bre] and [87Ros] (see also [84Pan]). These results are listed in Table 12.

Tabular Data

The thermodynamic properties of all the As species are listed in Tables 3, 8-12 in the format used in [82Pan] and [84Pan]. The equilibrium constant K_p is in terms of atmospheres (1 atm = 101 325 Pa) to the proper exponents as required by each formation reaction. The use of such tables is presented in detail by [84Pan].

Table 13 is somewhat unusual, because it contains the data for pure liquid As under various pressures of its own gas phase, whereas the usual choice of standard state is the liquid under 1.013 bar of pressure, which is nonexistent for As. The table permits computation of similar data for $\text{As}(\text{g})$, $\text{As}_2(\text{g})$ and $\text{As}_3(\text{g})$, formed from $\text{As}(\text{L})$. For example, if it is desirable to compute $\Delta_f G^0$ for $\text{As}(\text{L}) \rightarrow \text{As}(\text{g})$ at 1500 K, it is sufficient to add $1/4 \Delta_f G^0 = -14\,681$ J/g-atom from Table 13 to $\Delta_f G^0 = 108\,812$ J/mol in Table 9 to obtain $\Delta_f G^0 = 94\,131$ J/g-atom which yields 5.3×10^{-4} bar of $\text{As}(\text{g})$ in equilibrium with liquid As.

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* Indicates key paper.

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